

## EFFECTS OF DISSOLVER SOLIDS ON SRC-I REACTION RATES

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Scaling up to the commercial-size, 6,000-ton-per-day, coal dissolver that will be installed in the SRC-I Demonstration Plant will be based on data from smaller dissolvers in the pilot plants at Wilsonville, Alabama and Ft. Lewis, Washington. At Wilsonville, researchers have known for several years that mineral-rich solids accumulate in the dissolver but are uncertain about whether solids will also accumulate in commercial dissolvers, which operate at higher velocities.

Commercial dissolver designs propose gas and slurry velocities about 10 times greater than those at Wilsonville, velocities that would impede solids from accumulating. Moreover, any solids that did build up would consist of larger particles than those at Wilsonville; larger solids would lead to less activity per weight due to less surface area exposed.

No clear experimental data exist to establish the effects of the accumulated solids. If they have no effect, the commercial scale-up problem is straightforward. If, however, they do have a catalytic effect on coal conversion by augmenting the reaction, then that effect should be quantified in order to determine the dimensions and design of commercial dissolvers. International Coal Refining Co. (ICRC) suspects that, without possible catalytic effects due to the solids, the yields of lighter coal liquid products may decrease.

To solve this problem, ICRC has been adding solids to the feed slurry, coal and solvent, to the continuous stirred tank reactor (CSTR) of its coal process development unit (CPDU). Actual Wilsonville dissolver solids were unavailable because Wilsonville now operates in a solids-withdrawal mode, and neither Wilsonville nor ICRC could produce enough washed and dried solids from the very dilute blowdown slurry. Therefore, Wilsonville filter cake and Kerr-McGee ash concentrate (K-MAC) were used to simulate dissolver solids. Similar results were anticipated, because both should contain the same mineral forms, pyrrhotite rather than pyrite and partially dewatered clay. However, filter cake and, particularly, K-MAC contain more reactive carbon compounds, unconverted coal and SRC, than true dissolver solids. Therefore, conversion of these reactive materials must be accounted for when calculating net product yields and kinetic constants.

Difficulties associated with pumping and processing feed slurries containing more than 45 wt % solids limit residue concentrations to 15 wt % maximum added to 30 wt % coal slurry. Thus, whereas solids in the Wilsonville dissolver are commonly found at the 20-30 lb/ft<sup>3</sup> level or higher, in the CPDU the maximum concentration is about 10-15 lb/ft<sup>3</sup>.

### EXPERIMENTAL PROGRAM

#### Materials

The coal is Kentucky #9 coal from the Pyro mine in Union County (Table 1). The filter cake and K-MAC are the mineral-rich residues from processing different Kentucky #9 coals in Wilsonville runs 175 and 167, respectively. Table 2 compares the composition of these residues to that of a typical dissolver solids sample taken from Wilsonville run 204. Although the filter cake and dissolver solids have similar total ash content, the dissolver solids contain over three times as much iron. K-MAC contains roughly half the ash in the other residues due to its very large preasphaltene content.

The solvent is Wilsonville process solvent (WPS) from run 179. It is a relatively good hydrogen-donor solvent, based upon results of the Wilsonville microautoclave test of solvent quality, which converted 74 wt % of a standard coal to tetrahydrofuran-soluble products.

### Reaction Conditions

The feed slurries consisted of 30% coal/70% WPS; 20% coal/15% filter cake/45% WPS and; 30% coal/15% K-MAC/45% WPS. Each slurry was processed at demonstration-plant design conditions: 2,000 psig, 840°F, liquid hourly space velocity of 1.4 hr<sup>-1</sup>, and a hydrogen feed rate equal to 3 wt % of the total slurry feed. Feed slurries of 30% coal/70% WPS and 20% coal/15% filter cake/45% WPS were also processed at reaction temperatures of 815 and 865°F, in order to calculate activation energies for the coal conversion reactions.

### Analytical Procedures

The solvent-extraction procedure of Schweighardt and Thames (1) separates starting solvent and product slurry samples into oil, asphaltene, preasphaltene, and residue fractions. Each fraction was analyzed for C, H, O, N, S, and ash to compute elemental balances and the hydrogen gas consumption. The quantity of residue in the product was adjusted to force the ash balance to equal 100%; these adjustments were minor, because the uncorrected ash balances were generally excellent.

### Statistical Analysis of Results

Experimentally observed effects of adding filter cake or K-MAC to the feed slurry were evaluated with the Student t-test to determine if the effects were statistically significant at the 95% confidence level. Replicate analyses of the samples discussed in this report, as well as previous samples (2), were used to compute an estimated variance for each analysis. Because most variances were based on only 12-17 degrees of freedom, the Student t-test was used to evaluate the statistical significance of the experimental results.

### Results

Because the residue additives contain SRC and unconverted coal in addition to potentially catalytic coal minerals, they could affect net product yields by entering the coal conversion reactions as either reactants or catalysts. Either mechanism enhances the oil and asphaltene yields and would be valuable to later SRC processes that recycle residue to the feed slurry. However, dissolver solids, which contain no reactive carbon, influence coal conversion only if the coal minerals are catalytic. To differentiate between the catalytic and reactant effects of the residues, first-order kinetic rate constants, based upon the assumed sequential reaction, were calculated:



This simple model correlates past data as well as more complex models with parallel reaction paths.

### Effect of Adding Slurry at Demonstration-Plant Conditions

Table 3 summarizes all data points in the study; the base condition without added residue was run twice, but the cases with added filter cake and K-MAC were run three times. The mean of the data values for each case is shown in Table 3a. Differences from the base case that are statistically significant at a 95% confidence level are underscored. In calculating the yield, the residue additives are treated as nonreactants, i.e., the yield of a species is calculated as the difference in percent of product minus percent of feed, divided by the percent of coal in the feed.

Effect Upon Product Slate. The combined net yield of the most desirable products, oils and asphaltenes, increased by 11 wt % moisture-and-ash-free (MAF) coal when 25 wt % filter cake was added and by 24 wt % MAF when an equal quantity of K-MAC was added. Both additives significantly reduced the net preasphaltene yield. K-MAC, but not filter cake, significantly reduced the net residue yield. Although

both additives improved oil yield, this change was statistically insignificant. Neither additive increased the yield of hydrocarbon gases.

Effect Upon Kinetic Rate Constants. Adding filter cake caused a statistically significant increase in  $k_2$ , the kinetic constant for converting preasphaltenes to asphaltenes. The increase from 2.7 to 4.2 hr<sup>-1</sup> is more than 50%. Adding K-MAC increased the reaction rate, but not enough to be statistically significant. The lesser catalytic activity of K-MAC is reasonable, because K-MAC has half the mineral content of filter cake, and petrographic analyses reveal most of the mineral surface area in the K-MAC is covered by preasphaltenes.

These results indicate that coal minerals in filter cake and K-MAC do not catalyze the conversion to lighter products of coal or oil.

Effect Upon Hydrogen Consumption. At the SRC-I Demonstration Plant, process solvent will be distilled from reaction products and continuously recycled, so that the solvents in the feed and product slurries have identical composition. The total hydrogen consumed by coal conversions must equal the amounts of hydrogen gas consumed. This theory is not true in CPDU experiments, because solvent is not recycled and therefore, may be a net donor or consumer of hydrogen.

When residue is not added to the feed, hydrogen content in the solvent drops from 8.2 to 7.9% during reaction. Nearly half the total hydrogen consumed in converting coal, 1.8 wt % MAF, was drawn from the solvent's hydrogen. Adding filter cake or K-MAC to the feed maintained or increased the solvent's hydrogen content during the reaction.

Filter cake and K-MAC promote hydrogen gas consumption, presumably by catalyzing solvent hydrogenation. Hydrogen gas consumption increases from 1 wt % MAF with no additive to 2.3 and 2.5 wt % MAF, if K-MAC and filter cake are added, respectively. These changes are twice as large as necessary to be statistically significant at a 95% confidence level.

The total hydrogen consumed in coal conversion is the sum of hydrogen gas consumption plus the net loss of hydrogen by the solvent, expressed as % MAF/coal. Total hydrogen consumption increased from 1.8 to 2.3 wt % MAF when either residue was added. This change is statistically significant.

#### Effect of Reaction Temperature

Liquefying 30% coal/70% WPS and 30% coal/15% filter cake/55% WPS was evaluated at reaction temperatures of 815, 840, 865°F; all other process conditions were fixed at demonstration-plant conditions. Table 4 summarizes the results.

Effect Upon Product Slate. Higher reaction temperatures increase oil yields, with or without filter cake. However, the change is statistically significant only with added filter cake. Higher reaction temperature significantly reduces preasphaltene yield, in spite whether filter cake is added. Coking seems not to be a problem at reaction temperatures of up to 865°F, because the lowest residue yields occurred at the hottest reaction temperature. These reported differences in residue yield are insignificant at a 95% confidence level.

At each reaction temperature, adding filter cake increased oil yield and reduced preasphaltene and residue yields. Hydrocarbon gas yield remained unaffected by adding filter cake.

Effect Upon Hydrogen Consumption. As reaction temperature increases, both hydrogen gas consumption and the total hydrogen consumed in coal conversions increase. However, hydrogen consumption seems less affected by reaction temperature, if filter cake is added.

Effect Upon Kinetic Constants. Adding filter cake increases the kinetic rate constant for preasphaltene conversion,  $k_2$ , at each reaction temperature. In addition, it lowers the activation energy for the reaction:

$$k_2 \text{ (no filter cake)} = 1.5 \times 10^{-7} \exp (-20,200/T)$$

$$k_2 \text{ (filter cake)} = 8 \times 10^{-4} \exp (-12,900/T)$$

In these equations, the temperature is measured in degrees Rankine.

For asphaltene conversion, the kinetic constant,  $k_3$ , is roughly 20% greater at each temperature when filter cake is added. However, the activation energy is about 52,500 Btu/lb-mol, in spite of whether filter cake is added. The increase in  $k_3$  is statistically significant only at an 80-90% confidence level.

Activation energy for cracking oils to hydrocarbon gas is about 77,000 Btu/lb-mol, without adding filter cake; however, when filter cake was added the activation energy was not calculated, because the data at 815°F seemed wrong.

## CONCLUSIONS

Filter cake catalyzes preasphaltene conversion and process-solvent hydrogenation. The kinetic rate constant for preasphaltene conversion increased by 50%; hydrogen gas consumption increased by a factor of 2.5. These changes are statistically significant at a 95% confidence level. Weaker evidence suggests filter cake may catalyze asphaltene conversion. Kerr-McGee ash concentrate is less catalytic than filter cake, apparently because it contains fewer coal minerals than filter cake, and preasphaltenes cover most of its mineral surface. Results of these analyses indicate that dissolver solids are catalysts in the SRC-I process and may be more active per unit mass than filter cake or K-MAC.

Filter cake and K-MAC contain SRC and unconverted coal that will react in the dissolver. A second-generation SRC process that recycles filter cake or K-MAC could improve coal conversion and reduce SRC lost to the ash residue. These improvements can be made without increasing gas by-products or reducing efficient hydrogen consumption.

## REFERENCES

- (1) Schweighardt, F. K, and B. M. Thames. August 1978. Solvent extraction of coal-derived products. Anal. Chem 50(9):1381.
- (2) Skinner, R. W., E. N. Givens, I. S. Kingsley, and F. K. Schweighardt. 1981. Effects of accumulated solids on dissolver performance. Pages 483-653 in Final SRC-I quarterly technical report, Vol. 2, April-June 1981. International Coal Refining Co., Allentown, Pa.

Table 1

Analyses of Kentucky No. 9, Pyro, Feed Coal

	Analysis
Moisture (wt %)	1.8
Volatiles (wt %)	36.1
Fixed carbon (wt %)	50.4
ASTM <sup>a</sup> ash (wt %)	13.1
Carbon (wt %)	70.4
Hydrogen (wt %)	4.8
Nitrogen (wt %)	1.5
Sulfur (wt %)	3.3
Sulfate S (wt %)	0.04
Pyrite S (wt %)	1.6
Oxygen (wt %)	6.1
Aluminum (wt %)	1.5
Silicon (wt %)	3.7
Iron (wt %)	1.5
Titanium (ppm)	570
Boron (ppm)	590
Chlorine (ppm)	2,400
Calcium (ppm)	80
Magnesium (ppm)	850
Potassium (ppm)	2,700
Sodium (ppm)	470
Pyridine soluble (wt %)	16.5

<sup>a</sup> ASTM, American Society for Testing and Materials.

Table 2

Analyses of Residue from Kentucky No. 9, Pyro, Feed Coal

Analysis	Residue type		
	Dissolver solids	Filter cake	K-MC
Elemental			
Carbon (wt %)	36.2	38.2	62.0
Hydrogen (wt %)	1.8	2.7	3.7
Nitrogen (wt %)	0.6	0.6	1.5
Sulfur (wt %)	8.1	3.3	2.3
Oxygen (wt %)	4.5	4.3	5.2
ASTM ash (wt %)	48.9	50.7	26.4
Iron (wt %)	21.9	6.16	2.75
Titanium (wt %)	0.22	0.11	0.11
Silicon (wt %)	6.03		
Aluminum (wt %)	3.09	5.59	2.46
Boron (ppm)	17,200	8,400	9,100
Calcium (ppm)	300	30	20
Magnesium (ppm)	2,100	300	980
Sodium (ppm)	26,600	17,600	15,900
Potassium (ppm)	9,100	14,700	4,800
Chlorine (ppm)	11,800		
Solubility fractions (wt %)			
Oils	0.0	16.0	0.0
Asphaltenes	0.0	3.0	2.0
Preasphaltenes	?	5.0	45.0
Residue		76.0	53.0

<sup>a</sup> Methylene chloride washed, normalized from 112%.

Table 3

Effect of Residue Addition at Demonstration Plant Reaction Conditions

	No additive	15% filter cake	15% K-MAC
Yield (wt % MAF)			
Total oil	16	24	25
Asphaltene	30	33	45
Oil and asphaltene	46	57 <sup>a</sup>	70
Preasphaltene	33	23	17
Residue	10	8	1
Hydrocarbon gas	6	6	6
Heteroatom gas	2	3	4
Water	2	3	2
Sulfur in SRC (wt %)	1.0	0.95	0.83
Hydrogen in oil (wt %)	7.9	8.3	8.2
Hydrogen consumed (wt % MAF)			
From H <sub>2</sub> gas	1.0	2.5	2.3
From (to) solvent	0.8	(0.2)	0.0
Total	1.8	2.3	2.3
Kinetic constants (hr <sup>-1</sup> )			
K <sub>1</sub>	14	6.6	9.4
K <sub>2</sub>	2.7	4.2	3.2
K <sub>3</sub>	1.4	1.5	1.3
K <sub>4</sub>	0.035	0.037	0.041

<sup>a</sup>Underlined values differ from the no additive case by an amount that is statistically significant at a 95% confidence level.

Table 4

Effect of Reaction Temperature on Coal Conversion

	No additive			15% filter cake		
	815°F	840°F	865°F	815°F	840°F	865°F
Yield (wt % MAF)						
Total oil	15	16	24	20	24	34
Asphaltene	30	30	23	33	33	24
Preasphaltene	38	33	28	28	23	20
Residue	11	10	10	9	8	7
Hydrocarbon gas	3	6	10	5	6	8
Heteroatom gas	2	2	3	2	3	3
Water	1	2	2	3	3	4
Hydrogen consumed (wt % MAF)						
From H <sub>2</sub> gas	0.9	1.0	2.0	2.0	2.5	2.5
From solvent	0.3	0.8	0.5	(0.2)	(0.2)	0.1
Total	1.2	1.8	2.5	1.8	2.3	2.6
Kinetic constants (hr <sup>-1</sup> )						
K <sub>1</sub>	2.0	2.7	3.7	3.2	4.2	4.9
K <sub>2</sub>	1.0	1.3	2.1	1.2	1.5	2.6
K <sub>4</sub>	0.017	0.034	0.053	0.030	0.037	0.055